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## Data Series 883

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# Methods

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Sampling of water included both underway continuous and discrete water samples, underway and station. These samples were analyzed either shipboard, onshore, or both, as noted in the descriptions.

## Shipboard Activities

### Underway Continuous Measurements (Sonde)

Using a YSI 6600 CTD, continuous measurements of temperature, salinity and pH at the seawater scale were collected during 12BHM01, 12BHM02, 12BHM03, 12BHM04 and 12BHM05 using a flow-through system located in the wet laboratory of the R/V *Weatherbird II*. The laboratory is equipped with a seawater flow-through system which pumps water from 1 meter below seawater surface into the lab. Water flowed continuously to the YSI sonde through tubing from the lab's flow-through nozzle into a bucket containing the instrument. Data values were logged at 5-minute (min) intervals. In addition, navigational, wind, salinity, temperature, and other data were also logged aboard the R/V *Weatherbird II*.

### Autonomous flow-thru (AFT) pH and CO<sub>2</sub>

The Sunburst AFT pH, which measures pH on the total hydrogen ion scale, was attached to the flow-through system. This system sampled the seawater every 3 minutes and has a precision and accuracy of 0.001 and  $\pm 0.003$ , respectively.

The Sunburst AFT-CO<sub>2</sub> system measured the partial pressure of CO<sub>2</sub> in water (pCO<sub>2</sub>) and was attached to the shipboard flow-through system. The instrument sampled every 5 minutes with a precision and accuracy of about 1 part per million (ppm) and  $\pm 3$  ppm, respectively.

### Discrete Surface Samples

Discrete water samples were collected while underway during each cruise following protocols outlined in Dickson and others (2007). Surface-water samples were collected every 2 hours (h) in biochemical oxygen demand (BOD) bottles for measurement of total alkalinity (TA) and total carbon dioxide (TCO<sub>2</sub>) on shore (see below).

### Discrete Vertical Profile Samples at Stations

Discrete samples from vertical profile casts were collected at station locations selected prior to the start of 11BHM01 and 11BHM02 ([Trackline](#)). For these casts, a 12-bottle Niskin rosette (20-L bottle volume) with an electronic trigger was fitted with a Sea-Bird SBE 911*plus* CTD and altimeter. The CTD provided salinity, temperature, depth, fluorescence, and dissolved oxygen data. The rosette was lowered to just above the sea floor, and bottles were filled at select depths as the rosette was brought to the surface. Water samples were collected from the Niskin bottles for TA, TCO<sub>2</sub>, and pH analyses.

## Shipboard pH Analyses

Discrete samples for shipboard analyses of pH were taken only at the stations. Approximately 30 milliliters (mL) of seawater was collected directly into cylindrical optical glass cells for pH on the total scale (pH<sub>T</sub>) measurements on the total hydrogen ion scale following the procedure of SOP6b (Dickson and others 2007). Once filled, cuvettes for pH were rinsed with distilled (DI) water, and placed into an aluminum cell warmer attached to a water bath at 25°C for approximately 30 min. Shipboard pH measurements were performed using an Agilent 8453 spectrophotometer, purified metacresol purple indicator dye, and equations modified by (Liu and others 2011).

## Discrete Surface Samples Analyzed Ashore

### Preserved Total Alkalinity and Total Carbon Analyses

Seawater samples were collected from the sampling manifold of the shipboard flow-through seawater system in 300-mL BOD bottles. Samples were preserved by adding 100 microliters (μL) of a saturated solution of mercuric chloride (HgCl<sub>2</sub>) and were sealed with a ground glass stopper lightly coated with Apiezon L grease. Samples were transported to the USGS Carbon Chemistry Laboratory in St. Petersburg, Florida. Total alkalinity samples were analyzed with an Ocean Optics USB 2000 spectrophotometer, bromol cresol purple indicator dye, and the methods of Yao and Byrne (1998). Total carbon was analyzed using the coulometric methods of Dickson and others (2007). Precision and accuracy for these methods was 1 micromole per kilogram (μmol/kg) for TA and TCO<sub>2</sub>.

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Page Last Modified: Thursday, September 18, 2014, 10:11:57 AM

